# 6 Recommendations

California's routine databases on emissions and ambient air quality are uncommon in their extent (number of monitors and years of operation) and in their high quality. In addition, many special studies that address air quality issues have been conducted in California. Data from these sources have already answered many questions concerning the ozone weekend effect. However, the objectives of routine programs and special studies have not specifically included understanding day-of-week differences in ozone and other pollutants. It is not surprising, therefore, that explaining the ozone weekend effect will require additional information to augment existing databases. Staff recommends that the current, highly successful, dual precursor control strategy for reducing ozone levels be maintained while conducting additional research to definitively identify the contributing causes of the weekend effect and to quantify their contributions.

This chapter presents a multi-disciplinary research program needed to resolve the cause(s) and implications of the ozone weekend effect. No area of research recommended below is likely to suffice by itself. Without a multi-faceted effort, the cause(s) and implications of the ozone weekend effect may remain ambiguous. Chapter 7 in the Technical Support Document provides additional detail concerning these recommendations as a starting point for discussion and planning.

## Recommendation #1: Update and extend laboratory data concerning alternative causes of the ozone weekend effect

Earlier experiments should be updated based on present-day conditions. New experiments should be conducted to address important alternative causes of the ozone weekend effect.

Many past experiments have already revealed important aspects of ozone-producing systems. However, these experiments were often designed from a generic perspective, and they may not be directly applicable to the ozone weekend effect. These experiments should be repeated based on the conditions found during any current or representative recent air quality studies.

- Evaluation of chemical mechanisms when VOC/$NO_X$ ratios and $NO_X$ concentrations are both low. The chemical mechanisms used in modeling applications need to accurately represent the chemical processes occurring under conditions observed on weekends and aloft in addition to the surface conditions on weekdays.

- Evaluation of heterogeneous chemical reactions involving $NO_X$ emissions and byproducts. A better understanding is needed of $NO_X$ products and how and when they are temporarily or permanently removed from the ozone photochemical system.

- Evaluation of chemical reactions involving sea salts (initially and primarily chlorides but also bromides) and potentially impacting the formation and destruction of ozone.

- Evaluation of $NO_X$-timing effects under current conditions (i.e., updating work portrayed in Figure 2-3).

- Evaluation, as possible, of potential effects associated with carryover aloft. For example, what are the impacts of the introduction of hydroxyl radicals in mid-morning associated with the chemical reactions aloft (photolysis of nitrous acid (HONO) and the reaction of ozone and water vapor) and the subsequent mixing into the surface layer?

- Evaluation studies of potential indicators and observation based methods (OBM) for characterizing conditions in which ozone is primarily sensitive to VOC or to $NO_X$. This is one of the most promising approaches for understanding the weekend effect, yet there has been no laboratory evaluation of indicators or OBMs.

- Evaluation of sources and sinks of free radicals (OH, $HO_2$, $RO_2$). The budgets of these species are critical for correct representation of both the production rate of ozone and the sensitivity of ozone to VOC and $NO_X$. Large uncertainties remain in the budgets of these species (e.g., Tonnesen, 1999) and they have not been measured in any of the chamber experiments that were used to develop current photochemical mechanisms.

In addition, new experiments should be carried out to identify and quantify a spectrum of air pollutants that could play significant roles in the ozone weekend effect. For example, HONO, $NO_2$, and $HNO_3$ all play potentially critical roles in the origin and fate of ozone. Other experiments might be designed to isolate important points that help discriminate between the alternative causes of the ozone weekend effect. For example, the “carryover near the surface” hypothesis might be evaluated, in part, by examining the specific reactivity of air near the surface on Friday, Saturday, Sunday, and Monday at 4 a.m. and at 8 a.m.

## Recommendation #2: Develop day-specific emission inventories to support efforts to model weekday-weekend differences in ozone

Emission inventories for each day of the week are needed to help determine the causes of the ozone weekend effect. These inventories must reveal in sufficient detail the quantity, the timing, and the location of VOC and $NO_X$ emissions for weekdays, for Fridays, for Saturdays, for Sundays, and for Mondays. Although desirable, separate inventories for the individual mid-week weekdays might not be necessary.

Day-of-week emission inventories are needed to support air quality models that simulate the ozone weekend effect. To date, emission inventories used in modeling

exercises comparing weekdays and weekends have been, of necessity, rather speculative. Day-specific hourly emissions are needed for stationary and area sources as well as for mobile sources.

Special emphasis may be needed for major source regions in the SoCAB, such as, the South Central area of Los Angeles. This area is a major source region for ozone precursors. The Lynwood monitoring site represents a broad, high emissions area in South Central Los Angeles, which has unusually high concentrations of CO (and presumably VOCs) on Saturday during the mid-day hours (Figure 5.3.40 in the Technical Support Document). Inventories for this and other areas may be crucial for resolving the cause(s) of the ozone weekend effect.

The recommendations in the Technical Support Document address work already planned or in progress and work that may be needed in addition to present plans. The major recommendations include the following:

- Acquire and analyze hourly summaries for on-road vehicle activity (especially surface street data to complement the extensive freeway data already being collected and analyzed) by vehicle class throughout the SoCAB.

- Quantify day-specific differences in emissions for important stationary-source and area-source categories.

- Analyze existing data by day-of-week from continuous emissions monitoring (CEM) systems at major industrial sources of $NO_X$ emissions.

- Quantify day-specific emissions for significant source regions, such as South Central Los Angeles.

## Recommendation #3: Design and execute modeling studies that address alternative hypotheses concerning the cause(s) of the ozone weekend effect

Modeling exercises would use the new day-specific emission inventories to investigate how the mix of primary and secondary pollutants affects ozone formation on weekdays and on weekends.

Dynamic simulation models such as the Urban Airshed Model (UAM) are important tools for comparing alternative strategies for reducing emissions. Modeling exercises should be used to compare and contrast the effects of periodic emission reductions on weekends to the effects of strategic emission reductions on all days. Only models can make such comparisons because the strategic reductions have not yet occurred.

Effective and reliable simulations require satisfactory agreement between model predictions and appropriate “base cases.” The modeling exercises recommended here should not be carried out until such base cases have been developed based on

the recommended improvements in air quality and emissions activity data. The base cases should be capable of reproducing the salient features (e.g., double diurnal ozone peaks in the eastern basin, ozone concentrations in the central basin, ozone concentrations aloft) that indicate the model is properly handling atmospheric processes critical to assessing hypotheses of the ozone weekend effect. When satisfactory base cases characterizing day-of-week emissions are available, a carefully designed series of modeling exercises would be run.

These exercises should include the following tasks:

- Compare modeled concentrations of pollutants aloft with measured concentrations observed in field studies. A minimal effort might use SCOS97 data for this task.
- Conduct model performance evaluations specifically with respect to factors that are relevant to the alternative hypotheses in Chapter 2.
- Model the effects of different sequences of weekday (WD), Saturday (SA) and/or Sunday (SU), emissions.
- Model the effects of different sequences of "future" WD, SA, and SU emissions that represent strategic emission reductions. These exercises should ensure that the initial conditions, the boundary conditions, and the modeled concentrations aloft appropriately reflect the lower "future" emissions.
- Compare model results that help discriminate between the alternative causes of the ozone weekend effect. For example, the $NO_X$-reduction hypothesis could be evaluated by comparing a present-day sequence of WD, SA, SU, WD to a sequence of "future" weekdays, WD1, WD2, WD3, WD4 (where WD1=WD2=WD3=WD4=(SA + SU)/2. If the $NO_X$-reduction hypothesis is correct, then ozone levels on the present-day SA and SU should be similar to the ozone levels on the "future" WD2 and WD3, respectively.

## Recommendation #4: Conduct a field study to augment existing ambient air quality databases in the South Coast Air Basin

Existing databases for ambient air quality must be augmented in several respects before the alternative cause(s) of the ozone weekend effect can be resolved.

An expansion of routine sampling methods alone will help and should be pursued but will not suffice. Ultimately, issue-targeted field studies in the South Coast Air Basin is recommended to gather the needed ambient air quality data (including data to refine understanding of atmospheric processes occurring above the routine surface-based measurements). Existing data bases should be thoroughly mined first to guide the final details of any field study efforts. A detailed outline encompassing a potential comprehensive field study, assuming sufficient resources, is presented in the Technical Support Document.

- **Location and duration**

The field study ideally would take place in the South Coast Air Basin over 18 months comprising two May-October "ozone" seasons for addressing the ozone weekend effect and one November-April "winter" season for addressing associated effects on particulate matter.

- **Scope and resolution of surface air quality measurements**

For every day of the study, hourly surface measurements would include accurate speciation of VOCs, accurate quantification of NMOC, $NO_X$, NO, $NO_2$ (direct measurement, not $NO_X$ – NO difference), total reactive nitrogen ($NO_Y$), ultraviolet sunlight, and PM2.5 (including elemental carbon). NMOC data, in addition to VOC species, are needed to capture the contribution of oxygenated reaction products of VOC emissions. Each of these measurements would be taken to represent major subregions of the SoCAB. Measurements should be made using artifact-free methods that can be deployed in the field.

For at least 15 weekday-weekend transitions (Fri.-Sat.-Sun.-Mon.) during the ozone seasons, hourly measurements would include HONO, $NO_2$, $HNO_3$, nitrates, nitrate radical ($NO_3$), PAN, and also hydrogen peroxide ($H_2O_2$) and organics to help evaluate VOC and $NO_X$ sensitivities.

- **Scope and resolution of air quality measurements "aloft"**

For the same 15 weekday-weekend transitions (Fri.-Sat.-Sun.-Mon.) with augmented surface measurements, additional measurements aloft would include the following: accurate speciation of VOCs, accurate quantification of NMOC, $NO_X$, NO, $NO_2$ (direct measurement, not $NO_X$ – NO difference), total reactive nitrogen ($NO_Y$), ultraviolet sunlight, and PM2.5 (including elemental carbon).

Measurements would be collected hourly during daylight hours and 2 to 4 times during the nighttime hours.

For all sampling periods, measurements would be taken at three or more heights between 50 meters and 1000 meters at four or more locations.

The sampling periods would include a wide spectrum of conditions rather than limiting attention to ozone "episodes." Nevertheless, anticipated ozone maxima should be 70 ppb or more each day at most locations in the basin.

Measurement methods should be artifact-free and as comparable to surface measurement methods as possible.

- **Day-specific hourly profiles for VOC species**

Measurements of VOC species, including oxygenated species, such as formaldehyde and acetaldehyde, should be included frequently enough to determine

differences in day-specific hourly profiles for VOCs. Accurate day-specific profiles are needed to address issues relating to carryover of pollutants, source apportionment, and differences in reactivity.

- **Contributions of carryover aloft to surface measurements**

For the same 15 weekday-weekend transitions (Fri.-Sat.-Sun.-Mon.) with augmented surface measurements, tracers would be released aloft before sunrise. Surface measurements of these tracers would help determine how pollutants that carry over aloft contribute to surface measurements the following day.